Journal of Thermal Analysis, Vol. 6 (1974) 473—477

SPECIAL FEATURES OF THE COMPENSATION EFFECT IN NON-ISOTHERMAL KINETICS OF SOLID-PHASE REACTIONS

A. V. NIKOLAEV, V. A. LOGVINENKO and V. M. GORBATCHEV

Institute of Inorganic Chemistry, Siberian Department of the Academy of Sciences of the U.S.S.R., Novosibirsk, U.S.S.R.

(Received November 22, 1972)

The appearance of the compensation effect ($\log A = a + bE$) in non-isothermal kinetics of solid-phase reactions is discussed.

An analytical expression of the compensation effect is derived in the form

$$\ln A = \ln \frac{E\left(\frac{dT}{dt}\right)_s}{RT_s^2} + \frac{E}{RT_s}$$

It is demonstrated that the compensation effect appears in a number of chemical reactions if the T_s and rate constant values are close. Experimental data confirm the theoratical discussion.

In a number of chemical reactions whose rate constants are satisfactorily described by the Arrhenius equation

$$K = A \exp\left(\frac{-E}{RT}\right) \tag{1}$$

the so-called *compensation effect* [1] is sometimes observed:

$$\log A = a + bE \tag{2}$$

This effect is also known in isothermal decompositions of solid substances and in catalytic reactions. A more generalized inspection reveals the existence of an interrelationship between the changes in three quantities, namely A, E and ΔT, the temperature range in which the solid-state reaction proceeds at a measurable rate [2]. The linear relationship described by Eq. (2) is observed when changes in decomposition conditions (dispersity, pressure of the gaseous reaction product, etc.) do not result in a noticeable change of ΔT.

The value of a is usually close to zero [2].

Several explanations exist for the compensation effect observed in isothermal processes. Some researchers consider this effect apparent [3].

The appearance of the compensation effect in the kinetics of non-isothermal reactions has not yet been studied in detail.

The rate of a solid-state chemical transformation under non isothermal conditions can be written for various process mechanisms (interface reactions, growth of nuclei, diffusion) in the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K(1 - \alpha)^n \tag{3}$$

where α is the conversion and n the formal order of the reaction. By combining Eq. (3) with the Arrhenius equation, we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(1 - \alpha)^n \exp\left(\frac{-E}{RT}\right) \tag{4}$$

In all cases, the dependence of the conversion rate $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ on time t is expressed by a curve having a maximum at the temperature T_s ($\alpha = \alpha_s$). At the maximum

$$E = \frac{nRT_s^2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_s}{q_s(1 - \alpha_s)}$$

Let us substitute Eq. (4) for the point α_s into the above equation. After simple transformation, we arrive at the following expression for the rate constant:

$$K = \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_s (1 - \alpha_s)^{1-n}}{RT_s^2 \cdot n} \exp\left(\frac{E}{RT_s}\right) \exp\left(\frac{-E}{RT}\right) \tag{5}$$

The value of $\frac{\mathrm{d}T}{\mathrm{d}t}$ is close to the value of the heating rate q (°C/sec).

In accordance with Eq. (5), the value of the preexponential factor is

$$A = \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_s (1 - \alpha_s)^{1-n}}{RT_s^2 \cdot n} \exp\left(\frac{E}{RT_s}\right) \tag{6}$$

Since $\frac{(1 - \alpha_s)^{1-n}}{n} \approx 1$ [4, 5], we finally obtain

$$A = \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_s}{RT_s^2} \exp\left(\frac{E}{RT_s}\right); \quad \ln A = \ln \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_s}{RT_s^2} + \frac{E}{RT_s} \tag{7}$$

Eq. (7) is the analytical expression of the compensation effect for non-isothermal kinetics.

Thus, for a given substance, the compensation effect appears when $\left(\text{at constant } \frac{\mathrm{d}T}{\mathrm{d}t}\right)$ a change in the decomposition conditions (dispersity, gas pressure) leads to a change in E, but to only a slight change in T_s.

This finding allows the treatment of the slight change in the value of T_s in non-isothermal kinetics as the basis of maintaining the constancy of the temperature range ΔT and the appearance of the compensation effect in isothermal kinetics.

For a number of chemical reactions, the compensation effect will be observed if $\left(\text{at}\ \frac{dT}{dt} = \text{const.}\right)$ the T_s values are close (leading to the constancy of b in Eq. (2) and the values the of rate constants are close (ensuring the constancy of a in Eq. (2)).

By way of example for the first case, we shall consider the dehydration of the magnesium EDTA chelate:

$$Mg_2L \cdot 9H_2O \rightarrow Mg_2L + 9H_2O$$

This reaction was carried out in a continuous reactor (of the gas chromatograph type, fitted with a bypass instead of columns) allowing control of the rate of flow of nitrogen through the sample (10 mg) in an ampoule with a porous bottom. The results are presented in Table 1.

At low flow rates of the gas (~5 ml/min) the dehydration reaction (more precisely, the reversible deaquation and substitution of ligands) proceeds in an atmosphere of the released water vapour. At flow rates of $\geq$40 ml/min the dehydration conditions may be assumed to be close to the conditions of constantly maintained vacuum [6]. The change in the nitrogen flow rate will therefore change the shape of the kinetic curve, i.e. the value n of the formal order of reaction.

Table 1

Kinetic parameters of the dehydration of the magnesium EDTA chelate $Mg_2L \cdot 9H_2O$ ($q = 0.1$ °C/min) $\log A = 0.5\,E - 3.5$

Parameters	Nitrogen flow rate, ml/min					
	6	10	15	20	25	40
T_s, K	448	423	409	420	418	398
n	0.75	1.1	1.2	1.5	1.9	2.0
E, kcal/mole	18.7	21.1	22.4	24.4	24.9	24.6
$\log A$	5.2	6.8	7.7	8.3	8.6	9.0

The compensation effect appears under the conditions of a corresponding increase of the effective energy of activition E on the increase of the formal order of reaction n. The curve $E = f(n)$ then proceeds close to the theoretically expected course [7, 8], corresponding to the formula $E_i \cdot \frac{1 - \alpha_{si}}{n_i \cdot \alpha_{si}} \approx E_0$, where E_0 is some definite minimum energy of activation of the chemical reaction for $n \rightarrow 0$. For endothermic processes corresponding to the scheme $A_s \rightarrow B_s + C_g$, the value of E_0 is close to the enthalpy of the process.

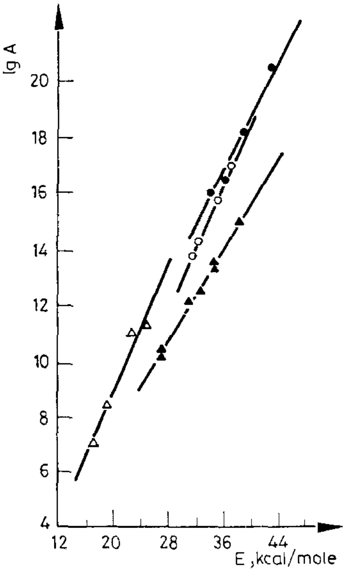

Fig. 1. Compensation effect in the dehydration of rare earth succinates and maleates: ○ — rare earth maleates; ● — lanthanum, cerium, erbium and ytterbium succinates; △ — praseodymium–holmium succinates (first dehydration stage); ▲ — praseodymium–holmium succinates (second dehydration stage)

By way of example for the second case, Fig. 1 illustrates calculations based on literature data [9, 10] for the dehydration of rare earth maleates and succinates having close values of T_s and rate constants.

References

1. B. I. Peschevitsky and V. P. Kazakov, Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim., No. 7, Issue 2 (1963) 20.
2. M. M. Pavlyuchenko, E. A. Prodan and S. A. Slyshkina, Dokl. AN SSSR, 181 (1968) 1174.
3. B. I. Peshchevitsky and S. P. Khranenko, Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. No. 2, Issue 1 (1972) 18.
4. T. V. Meshcheryakova and N. D. Topor, Vestn. Mosk. Gos. Univ., Khimiya, No. 3 (1967) 73.
5. H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1964.
6. M. M. Pavlyuchenko, E. A. Prodan and S. A. Slyshkina, Geterogennye khimicheskie reaktsii, Izd. Nauka i Tekhnika, Minsk (1970) 105.
7. V. M. Gorbatchev and V. A. Logvinenko, Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. No. 12, Issue 5 (1971) 20.
8. A. V. Nikolaev, V. A. Logvinenko, V. M. Gorbatchev, L. J. Myakhina and N. N. Knyazeva, Proc. 3rd Internat. Conf. Thermal Anal, Switzerland, 1971.
9. V. P. Sevostyanov and L. M. Dvornikova, Zh. Neorgan. Khim., 16 (1971) 1812.
10. V. P. Sevostyanov and L. M. Dvornikova, Zh. Neorgan. Khim., 17 (1972) 1499.

Résumé — On discute l'apparition de l'effet de compensation ($\lg A = a + bE$) sur la cinétique non-isotherme des réactions en phase solide.

On propose une expression analytique de l'effet de compensation sous forme de l'équation

$$\ln A = \ln \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{s}}}{RT_{\mathrm{s}}^{2}} + \frac{E}{RT_{\mathrm{s}}}$$

On démontre que l'effet de compensation apparaît pour un certain nombre de réactions chimiques si les valeurs de T_{s} et des constantes de vitesse sont voisines. Des données d'expérience viennent à l'appui de la discussion théorique.

Zusammenfassung — Das Auftreten des Kompensationseffektes ($\lg A = a + bE$) in der nicht-isothermen Kinetik von Festphasenreaktionen wird erörtert.

Ein analytischer Ausdruck des Kompensationseffektes wird in Form der Gleichung

$$\ln A = \ln \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{s}}}{RT_{\mathrm{s}}^{2}} + \frac{E}{RT_{\mathrm{s}}}$$

abgeleitet.

Es wird bewiesen, daß der Kompensationseffekt bei einer Reihe von chemischen Reaktionen auftritt, wenn die Werte von T_{s} und die Geschwindigkeitskonstante nahe beieinander liegen. Versuchsangaben bestätigen die theoretischen Erwägungen.

Резюме — Рассмотрено проявление «компенсационного эффекта» ($\lg A = a + bE$) в неизотермической кинетике твердофазных реакций.

Получено уравнение

$$\ln A = \ln \frac{E\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{s}}}{RT_{\mathrm{s}}^{2}} + \frac{E}{RT_{\mathrm{s}}}$$

являющееся аналитическим выражением этого эффекта; показано, что компенсационный эффект наблюдается в случае близости величин T_{s} и констант скорости реакции у ряда химических реакций. Проведен эксперимент, подтверждающий теоретическое рассмотрение.